Aluminium Phosphate Frameworks with Clathrated Ethylenediamine: *X*-Ray Characterization of $Al_3P_3O_{11}(OH)_2{\cdot}N_2C_2H_8$ ($AlPO_4$-12)

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The structure of the $AlPO_4$-12 member of the open aluminophosphate frameworks consists of sheets of four-co-ordinate phosphorus and aluminium, $[Al^{IV}P^{IV}O_4(OH)]^-$, alternating, along [100], with slabs of four-co-ordinate phosphorus and five-co-ordinate aluminium, $[Al^{V}{}_2P^{IV}{}_2O_7(OH)]^+$, to form channels in [010] and [001]; the sheets and slabs are linked *via* Al–O–P linkages with ethylenediamine positioned between them in a fashion suggesting its structure-directing (template) role during synthesis.

Recently the synthesis of aluminophosphate frameworks,[1,2] some of which are analogues of the zeolite (aluminosilicate) molecular sieves,[3] has been reported. The family has been designated $AlPO_4$-*n*, where the suffix *n* denotes a specific structure type. Thus $AlPO_4$-20 is the analogue of the zeolite sodalite and $AlPO_4$-17 that of erionite; both have absorptive and molecular shape selective properties similar to that of the corresponding zeolite.

The synthesis of each framework is associated with a specific 'template' added to an aluminophosphate gel prior to its being heated between 150 °C and 250 °C under hydrothermal conditions.[1,2] As the term 'template' would imply, the compound added (typically an amine) is thought to act as a director, dictating the pore and channel geometry in these frameworks. When this agent is absent, no open frameworks are formed.[1,2] Reported here is the *X*-ray crystral structure of another member of this family, $AlPO_4$-12[$Al_3P_3O_{11}(OH)_2{\cdot}$en; en = ethylenediamine] synthesised by heating an aluminophosphate gel with overall composition $0.5C_2N_2H_8 : Al_2O_3 : P_2O_5 : 40H_2O$ at 200 °C for 36 h.

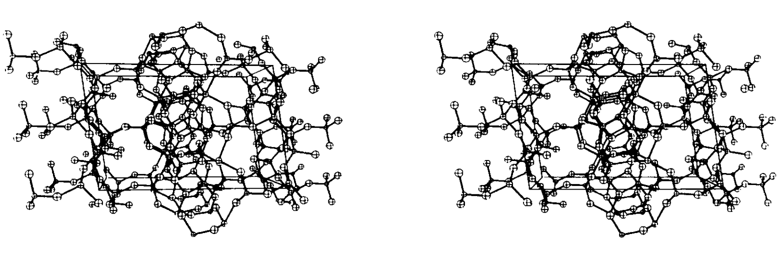

Figure 1. A stereoscopic ORTEP drawing of the crystal structure of $AlPO_4$-12 down [010]. The *z*-axis points across the page. Tetrahedal sheets (see text) containing aluminium and phosphorus are in (100) planes at $x = 0$ and $x = 1$. Five co-ordinate aluminium is segregated into the slab, also in (100), at $x = \frac{1}{2}$.

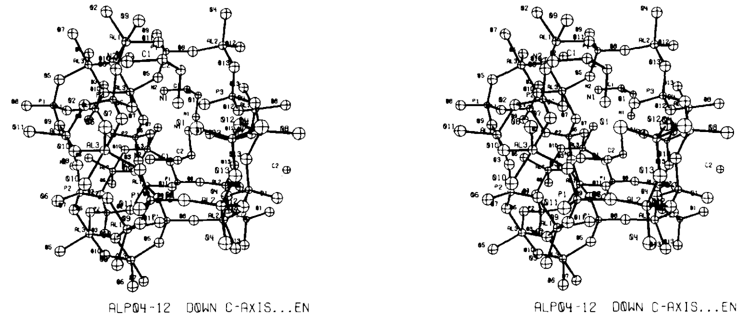

Figure 2. A stereoscopic ORTEP drawing, down [001], of the environment about ethylenediamine clathrated by the aluminophosphate framework of AlPO$_4$-12. The C(1)–N(2) bond points along the prominent channels in [100], (across the page). Selected average bond lengths are P(1)–O 2.53(1)Å, P(2)–O 1.53(1)Å, P(3)–O 1.54(1)Å, Al(1)–O 1.84(3)Å, Al(2)–O 1.74(1)Å, Al(3)–O 1.84(4)Å.

The structure† (Figures 1 and 2) consists of an open aluminophosphate framework which clathrates en. Channels, running parallel to [001] and [010], are formed by the linking of sheets of aluminium and phosphorus tetrahedra (T-sheets) and *x ca.* 0, and slabs of aluminium trigonal bipyramids and phosphorus tetrahedra at *x ca.* ½, *via* Al^{IV}–O–P^{IV} bonds (Figures 1 and 2). The Links are *via* aluminium in the T-sheets and phosphorus in the slabs. The T-sheets in the (100) plane are formed by the linking of four-membered rings of AlO$_4$ and PO$_4$ tetrahedra with strict alternation of Al and P. There are no Al–O–Al or P–O–P linkages within the sheet. Structurally, this element of AlPO$_4$-12 is related to those of AlPO$_4$-5 and AlPO$_4$-17, which consist of strictly alternating AlO$_4$ and PO$_4$ tetrahedral frameworks.[1,2]

The structure of the slab at *x ca.* ½ consists of groups of four aluminium centred trigonal bipyramids, cross-linked by PO$_4$ tetrahedra. The structural element is unknown in either the aluminosilicate molecular sieves[3] or the AlPO$_4$-family.[1,2]

Although not located in difference Fourier syntheses, OH groups may be associated with O(1), which only co-ordinates to one phosphorus atom [P(3)] and O(10) which is co-ordinated to three aluminium atoms (a similar grouping is found in [AlPO$_4$-15],[5] where the positions of the hydroxy groups were determined). The composition of the T-sheet and slab would then be [Al^{IV}P^{IV}O$_4$(OH)]$^-$ and [Al$^{V}_2$P$^{IV}_2$O$_7$(OH)]$^+$, respectively. A neutron powder diffraction study is being undertaken to determine the proton positions in AlPO$_4$-12.

The position and aspect of the en molecule is consistent with its exerting a structure-directing influence on the framework. It is arranged between the T-sheet and the slab with its C–N bonds directed along the channels (Figure 2). It is hydrogen bonded to the O(1) hydroxy group *via* N–H $\cdots$ O(1) [H $\cdots$ O(1) 2.0 Å] and N–H $\cdots$ O(1) [H $\cdots$ O(1) 2.17 Å] bridges.

In summary, AlPO$_4$-12 consists of sheets of [Al^{IV}P^{IV}O$_4$(OH)]$^-$ joined *via* P–O–Al bridges to slabs of composition [Al$^{V}_2$P$^{IV}_2$O$_7$(OH)]$^+$ to form channels parallel to [010] and [001]. These channels contain ethylenediamine which is hydrogen bonded to an hydroxy group on the sheet and arranged along the channels in the structure suggesting its influence as a structure-directing agent during crystal growth.

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References

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† *Crystal data:* for Al$_3$P$_3$O$_{11}$(OH)$_2$·H$_2$N[CH$_2$]$_2$NH$_2$, monoclinic, space group $P2_1/c$, a = 14.542(2), b = 9.430(2), c = 9.630(2) Å, β = 98.21(1)°, U = 1307 Å^3, D_c = 2.26 g cm^{-3}, μ(M$_0$-K_α) = 6 cm^{-1}, Z = 4, λ = 0.7107 Å, crystal dimensions 0.22 × 0.16 × 0.04 mm, R = 0.072, R_w = 0.074 for 1956 reflections with $I > \sigma(I)$ collected at 25 °C on a PICKER-FACSI diffractometer; solved and refined using SHELX-76;[4] H atom positions were calculated then refined. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.